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Production of biodiesel: A technical review

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ABSTRACT

The energy crises, particularly the fear of depletion of mineral oils are becoming a very serious issue. Non-oil producing countries are becoming the victim of the scenario. On the other hand the environmental pollution, green house effect, global warming and acid rain are also threatening the life. Biodiesel is a promising alternative fuel which can cater the problems. Vegetable oils can be used to substitute mineral diesel after reducing their viscosity and specific gravity. For this purpose different techniques are used. Among these, transesterification is frequently used as it is the most reliable, most feasible, and can be used to produce biodiesel easily.

The conversion efficiency of biodiesel via transesterification depends upon the nature of feedstock, amount and type of alcohol and catalyst, operating temperature, and reaction time. In this study the performance of alkaline, acidic, and enzymatic catalysts have been reviewed. Modern techniques of development of biodiesel i.e., use of microwaves and super critical alcohol have also been discussed critically.

Contents

1. Introduction

The rising cost and depletion of reserves of mineral oils are becoming the serious threat to the humanity, which have forced the scientists to find out the new avenues of energy resources. The reserves of oil and gas will be exhausted in 41 and 63 years respectively, if their use remains continue at the present pace [1]. Since the consumption of oil and gas is increasing exponentially, therefore these reserves will be depleted even earlier. The scientist are already working on the feasibilities and commercialization of solar, wind, and geothermal energies, and recycling of municipal wastes. European countries have planned to use 5.75% of biofuels by the end of 2010 and 10% by the year 2020 [2].

In the year 2007–2008, the total consumption of petroleum products in Pakistan were 11,528,722 TOE and out of which

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9,157,914 TOE was imported [1]. The major consumption of it was in transportation and power sectors: 47.4% in transportation sector and 40% in power sector [3].

According to the reports of international agencies there will be 53% increase in the demand of energy by the year 2030. It is anticipated that the petroleum demand will increase from 84.40 million barrels to 116.00 million barrels per day by 2030 in USA alone [4,5]. Researchers are also concentrating on the viability of vegetable oils, which are renewable, biodegradable, and nontoxic. Their flash point is higher which makes their storage, transportation, and handling easy. Various types of edible and non-edible oils, used cooking oils, and animal fats have sufficient potential to be used as fuel in compression ignition engines.

The awareness and strict compliance of environmental legislations are also forcing the scientists to adopt the means to reduce the pollutant emissions. These pollutants are serious threat to the environment [6]. The scientists have already proved that the exhaust emissions of the compression ignition (CI) engines, when they are fed with vegetable oils, in pure or blended form, contain a reduced amount of CO, CO_2, THC, venomous compounds, and poly aromatic hydrocarbons [7–12]. The exhaust emissions of the diesel engines are almost free from oxides of sulfur (SO_x) when their fuel is replaced by vegetable oils [13]. However there is an increase of 2–5% of NO_x. It is also reported that vegetable oils produce some unregulated harmful compounds like acetaldehyde and benzene [14].

The idea of using vegetable oil as a fuel is almost as old as the diesel engine itself. In 1900 in an exhibition in Paris, the renowned scientist Sir Rudolf Diesel used the peanut oil to run engine for several hours [15]. He was highly excited, and expressed that the time would come when the vegetable oil would be equally important fuel. During the period of 1930s and 1940s, particularly during the World War II, the vegetable oils were used in emergency to substitute diesel [16,17].

Some scientists tried to use straight vegetable oils in compression ignition engine but favorable results could not be found. The main issues were their high viscosity and low volatility which hindered the smooth combustion of these fuels. These unfavorable properties are responsible for the plugging of the fuel lines and fuel injectors, carbon deposits on piston rings, and fouling on the piston heads [18–22]. Generally, the vegetable oils have higher pour point and cloud point due to which these fuels are not suitable in the cold areas particularly in winter season [23,24]. The vegetable oils also contain many saturated and unsaturated compounds and have high iodine value which increases their oxidation rate. Hence long time storage of such oils is not feasible [25]. The cetane number of vegetable oils is also much higher than that of mineral oils, which reduces the ignition delay [26].

Schuchardt et al. reported that acrolein, a toxic compound, is formed when vegetable oil is combusted in the engine, which is basically due to disintegration of glycerol [27]. Hence the use of straight vegetable oil is not suitable.

The chemical structure of vegetable oils should be altered to reduce their molecular weight, viscosity, and specific gravity, and to make their properties comparable to diesel such that they may be used in diesel engines without any modifications to the engines. The modified product is called biodiesel and it has tremendous advantages over raw oils. It is recycle-able, environment friendly, and has better lubricant properties as compared to diesel particularly when it is compared with ultra low sulfur diesel [28–30].

In 1982, an international conference was held in North Dokato to discuss the main issues related to biodiesel i.e., the effect of fuel on engine performance and durability, cost of fuel, fuel specifications, additives, oil producing plants, oil seed processing and extraction, etc. [31].

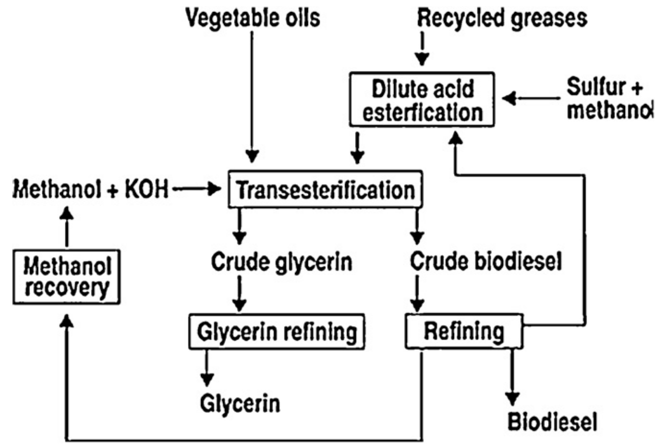


Fig. 1. Basic transesterification technology.

2. Transesterification

Several procedures have been established to convert vegetable oils into fuels which have properties comparable to diesel. These include transesterification, blending, cracking, micro-emulsification, and pyrolysis [9,32–35].

Transesterification is the most commonly used method for the development of biodiesel [9,35,36]. It has many advantages over other processes e.g., it is performed under normal conditions and it returns good yield of better quality biodiesel [37,38]. Hence transesterification technique has been reviewed in this article.

Transesterification is a chemical method in which the triglyceride is converted into diglyceride and diglyceride is converted into monoglyceride which is methyl or ethyl ester named as biodiesel. The reactions consist of consecutive reversible processes as shown below [9,39–41].

$$\text{Triglyceride} + \text{Alcohol} \rightleftharpoons \text{Diglyceride} + \text{R}'\text{COOR}$$

$$\text{Diglyceride} + \text{Alcohol} \rightleftharpoons \text{Monoglyceride} + \text{R}''\text{COOR}$$

In transesterification, alcohol is reacted with vegetable oil in the presence of appropriate catalyst. Generally ethyl or methyl alcohol is used consequently the ethyl/methyl esters are produced. After the reaction, two distinct layers of liquids i.e., ethyl/methyl ester and glycerin are appeared which are separated as shown in Fig. 1.

The vegetable oil is reacted with methanol already mixed with catalyst. The fluid is converted into crude biodiesel and crude glycerin. The glycerin is refined and disposed off for further use. The crude biodiesel is also refined and alcohol is separated from it which is reused in the cycle.

One molecule of vegetable oil/triglyceride reacts with three molecules of alcohol and produces three molecules of monoglyceride and one molecule of glycerol. The reaction is shown in Fig. 2 [42,43].

The byproduct of the reaction, the glycerol is also a useful product. It is used to prepare animal feed, carbon feedstock in

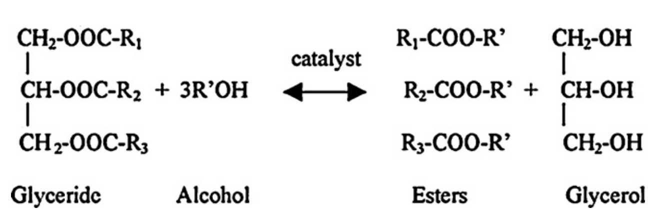


Fig. 2. Transesterification of vegetable oils [42,43].

fermentations, polymers, surfactants, pharmaceuticals and lubricants [44].

The rate of yield of biodiesel via transesterification depends upon many parameters. The most important of which are amount and type of alcohol, amount and type of catalyst, the reaction temperature, and reaction time. The moisture contents present in the feedstock and amount of free fatty acids also affect the yield.

Generally, the reaction is carried out at a temperature of 50–75 °C and completed within 2 h. Biodiesel and glycerol are separated gravitationally or centrifugally [45,46].

2.1. Feedstock for biodiesel

More than 300 feedstock have been identified which could be used to produce biodiesel. The conventional and non-conventional feedstock, used for the production of biodiesel, is shown in Table 1. These include edible oils, non-edible oils, wild oils, used cooking oils, and animal fats [47]. The most common vegetable oils are rapeseed, mustered, canola, sunflower, cotton seed, palm, soybean, linseed, corn, olive, coconut, hazelnut, pistachio,jatropha, honge, sesame, karanja, neam, mahu, caster, safallow, and jojoba oils [48–51]. Soybean oil is commonly used in USA, rapeseed oil in European countries, palm oil in Malaysia, and jatropha oil in India [52].

Dias et al. reported that the conversion efficiency of used oils (yellow grease) is lower than that of virgin oils. They converted the used and virgin, soybean and sunflower oils, and found that the yield was 92% and 97% for used and virgin oil respectively [53].

In 2003 Dmytryshyn et al. converted the neat canola oil and yellow grease, using methanol in the presence of base catalyst and reported that the conversion efficiency was 87% and 58% for neat canola oil and yellow grease respectively [54]. Whereas, Refaat et al. transesterified neat and used sunflower oil using methanol and KOH and concluded that the conversion efficiency for both the oils was same [55]. Alcantara et al. also reported that conversion efficiency is not affected by using neat or used oil, provided that appropriate amount and type of alcohol and catalyst is used [56].

Table 1
Conventional and non-conventional feedstock.

Conventional feedstock		Non-conventional feedstock
Mahua	Soybeans	Lard
Piqui	Rapeseed	Tallow
Palm	Canola	Poultry fat
Karang	Babassu	Fish oil
Tobacco seed	Brassica carinata	Bacteria
Rubber plant	Brassica napus	Algae
Rice bran	Copra	Fungi
Sesame	Groundnut	Micro algae
Safflower	Cynara cardunculus	Tarpenes
Barley	Cotton seed	Latexes
Coconut	Jatropha nana	Microalgae
Laurel	Jojoba oil	
Used cooking oil	Pongamiaglabra	

However the requirement of amount of catalyst is generally higher in case of used oil as compared to neat oil.

2.2. Chemical structure and properties

Vegetable oils and animal fats mainly consist of triglycerides and diglycerides with a small fraction of monglyceride. The chemical structure of these esters is compared with mineral diesel and biodiesel in Table 2.

The average chemical formula for common diesel fuel is $C_{12}H_{23}$. The vegetable oils consist of long chains with multiple branches resulting in molecules of large size. The molecular weight of vegetable oils ranges from 850 to 995, which is much higher than that of diesel which is 168 on average [58].

The kinematic viscosity and density of vegetable oils are much higher than those of diesel due to their higher molecular weight and complex structure. A comparison of various physical and chemical properties of diesel and of various vegetable oils is shown in Table 3.

The properties of biodiesel (BD) are comparable with mineral diesel. Hence it can be used as a fuel, in pure or blended form, in compression ignition engines. The fuel can be used without any

Table 2
Chemical structure of various esters [57].

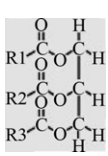
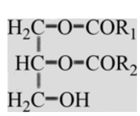
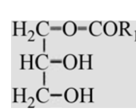
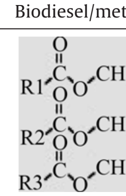
Fat and oil Triglyceride	Diglyceride	Monoglyceride	Biodiesel/methyl ester	Diesel
				$C_{12}H_{23}$

Table 3
Properties of various types of vegetable oils [59].

Vegetable oil	Kinematic viscosity at 38 °C (mm²/s)	Cetane no.	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Corn	34.9	37.6	39.5	−1.1	−40	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	−15	234	0.9148
Crambe	53.6	44.6	40.5	10.0	−12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	−15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	−6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133
Soya bean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161
Palm	39.6	42.0	–	31.0	–	267	0.9180
Babassu	30.3	38.0	–	20.0	–	150	0.9460
Diesel	3.06	50.0	43.8	–	−16	76	0.8550

Table 4
Physical and chemical properties of methyl esters and diesel [57].

Vegetable oil methyl ester	Kinematic viscosity (mm^2/s)	Cetane no.	Lower heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Peanut	4.9 (37.8 °C)	54	33.6	5	–	176	0.883
Soya bean	4.5 (37.8 °C)	45	33.5	1	−7	178	0.885
Babassu	3.6 (37.8 °C)	63	31.8	4	–	127	0.875
Palm	5.7 (37.8 °C)	62	33.5	13	–	164	0.880
Sunflower	4.6 (37.8 °C)	49	33.5	1	–	183	0.860
Tallow	–	–	–	12	9	96	–
Rapeseed	4.2 (40 °C)	5 l–59.7	32.8				0.882
Palm	4.3–4.5 (40 °C)	64.3–70	32.4	–	–	–	0.872– 0.877
Soybean	4.0 (40 °C)	45.7–56	32.7	–	–	–	0.880
Diesel	3.06	50	43.8	–	−16	76	0.855
20% BD	3.2	51	43.2	–	−16	128	0.859

Table 5
Physical and chemical properties of methyl esters and diesel [60].

Vegetable oil methyl ester	Viscosity (c St)	Density (g/L)	Flash point (K)	HHV (MJ/kg)
Cottonseed oil	3.75	871	455	41.18
Corn oil	3.62	873	427	41.14
Crambe oil	5.12	848	463	41.98
Hazelnut oil	3.59	875	425	41.12
Linseed oil	2.83	885	415	40.84
Mustard oil	4.1	866	442	41.3
Olive oil	4.18	860	447	41.35
Palm oil	3.94	867	434	41.24
Rapeseed oil	4.6	857	453	41.55
Safflower oil	4.03	866	440	41.26
Sesame oil	3.04	880	418	40.9
Soybean oil	4.08	865	441	41.28
Sunflower oil	4.16	863	439	41.33
Walnut oil	4.11	864	443	41.32

major modification to the engine. Singh et al. tabulated various properties of methyl esters of different vegetable oils and compared them with those of mineral diesel as shown in Table 4.

Ayhan also determined the properties of some methyl esters of various vegetable oils and made a comparison with those of mineral diesel as shown in Table 5.

Different oils return the biodiesel of similar chemical and physical properties when these are transesterified, provided that that suitable amount of alcohol and catalyst is used.

Banapurmath et al. compared the properties of methyl esters of honge (HOME), jatropha (JOME) and sesame oil (SOME) with diesel and their results have been reproduced in Table 6.

3. Use of catalysts

Transesterification process is carried out in the presence of catalysts. Both acid and base catalysts are used and their selection is made according to the characteristics of feedstock. The virgin vegetable oils, yellow grease (used cooking oil), or animal fats are reacted with alcohol in the presence of acid or base catalysts. The catalyst is used to expedite the reaction rate and to get better quality biodiesel [36]. The base catalysts are preferred over acid catalysts, owing to their capability of completion of reaction at higher speed, requirement of lower reaction temperature, and their higher conversion efficiency as compared to acid catalysts [62–65]. Fangrui et al. suggested that base catalyst is successful only when free fatty acid (FFA) is less than one [66]. Crabbe is of the view that base catalysts can also be used in case of FFAs greater than one but higher amount of catalyst is needed [67]. On the other hand, Fukuda et al. advocated that base catalysts exhibits excellent results when the FFA of oil is below two. They also reported that the rate of transesterification reaction becomes thousands times faster when base catalyst is used instead of acid catalyst [68]. Dorado et al. commented that the base catalysts are not successful for oils having FFA greater than 3 [69]. However, Gerpan reported that base catalysts could be effectively used for feedstock having FFA up to 5 [70].

Table 6
Properties of diesel, HOME, JOME, and SOME [61].

Property	Diesel	HOME	JOME	SOME
Density (kg/m^3)	840	870	870	882
Sp. gravity	0.84	0.87	0.87	0.882
Kinematic viscosity (c St) at 40 °C	3.5	5.5	5.65	5.34
Flash point (°C)	56	170	170	170
Calorific value (kJ/kg)	43,000	36,100	38,450	38,836

The base catalysts cause the sponification when they react with FFAs present in the vegetable oils or triglyceride, particularly when the acid value of feedstock is high [71]. In such cases acid catalysts are used.

The acid value of edible oils is normally low as compared to non-edible oils. However the acid value of edible oils also increases when they are used for frying purpose for long time. Tyagi et al. reported that the acid value of soybean oil increases from 0.04% to 1.51%, when it is heated at 190 °C for 70 h [72]. The acid value of rapeseed oil increases from 2 to 5.6 and that of palm oil increases from 5.6 to 20, when the oils are used for frying [73,74]. In such cases the use of acid catalysts shows better results.

3.1. *Base catalysts*

Base catalysts are popularly used to produce biodiesel, which are mainly divided into two types:

i. homogenous base catalysts
ii. heterogeneous base catalysts

3.1.1. *Homogenous base catalysts*

Various types of homogenous base catalysts are used for the transesterification of vegetable oils. The most common

among these are sodium hydroxide, sodium methoxide, potassium hydroxide, and potassium methoxide.

3.1.1.1. Sodium hydroxide. The use of sodium hydroxide as catalyst is preferred over potassium hydroxide because it makes less emulsification, eases the separation of glycerol, and is of lower cost [75,76].

Sinha et al. used sodium hydroxide, as catalyst, with methyl alcohol to convert the rice brawn into biodiesel. They varied the amount of catalyst and that of alcohol for various reaction temperatures and reaction times. They concluded that with methanol/oil molar ratio of 9 and 0.75% NaOH, maximum yield was obtained in 1 h at the reaction temperature of 55 °C [9].

Felizardo et al. reported that transesterified waste frying oil could be used as fuel to run the compression ignition engine. They suggested that methanol could be used to transesterify oil in the presence of NaOH. They proposed that one liter of methanol is sufficient for 4.8 l of oil, and 2.88 g NaOH will return the best results within 1 h. They performed all the experiments at 65 °C [77]. In 2008 Rashid et al. produced the sunflower methyl ester and optimized the affecting parameters. They reported that more than 97% yield could be obtained by using 1% NaOH and methanol/oil molar ratio of 6. They also concluded that suitable reaction temperature was 65 °C and time was 2 h [78].

Hoda used cotton seed oil to convert it into biodiesel and optimized the parameters which affect the yield of biodiesel. He employed methanol in the presence of NaOH by varying the methanol/oil molar ratio from 3 to 15 and amount of NaOH from 0.3 to 0.9%. He concluded that maximum yield could be obtained by employing methanol/oil molar ratio as 6 and amount of catalyst as 0.3% of oil at temperature of 60 °C with reaction time of 1 h [79].

Berchmans and Hirata transesterified crude palm and coconut oils to produce biodiesel. They varied the affecting parameters and concluded that the oils having low FFA should be base transesterfied using 1% NaOH and 28% methanol. They obtained 80% yield for palm oil and 55% for that of coconut oil [80].

Leung and Guo compared and optimized the parameters which affect the yield of biodiesel using neat canola oil and used frying oil. They reported that conversion efficiency for neat canola oil was 90.4%, when it was transesterified using methanol/oil molar ratio of 7 and 1% NaOH, maintaining the reaction temperature at 70 °C, and reaction time was 20 min. They further reported that the conversion efficiency could be increased up to 93.5% by decreasing the temperature from 70 °C to 40–45 °C but reaction time would be increased up to 60 min. They also revealed that optimum parameters for used frying oil were: methanol/oil molar ratio 7; 1.1% NaOH; reaction temperature 60 °C; and reaction time 1 h. The maximum yield was 88.8% [81].

Sharma and Singh conducted series of experiments on Jatropha curcus oil. They varied the amount of methanol, NaOH, reaction time, and reaction temperature and concluded that the maximum yield of 98% could be obtained by using 20% methanol and 1% NaOH at reaction temperature of 60 °C with minimum reaction time of 90 min [35].

Georgogianni et al. transesterified the used soybean oil and a mixture of soybean and cotton seed oil using methanol and sodium hydroxide. They concluded that the biodiesel produced from both the oils have much similar properties which were also comparable to mineral diesel [82].

Lubes and Zakaria compared the performance of two steps and single step transesterification processes and reported that 1% NaOH and methanol/oil molar ratio of 6 yielded more than 95% biodiesel when temperature was maintained at 60 °C and the reaction was completed in 1 h [83].

Table 7
Properties of diesel, karanja oil, and biodiesel [91].

Properties	ASTM test	Diesel	Karanja oil	Biodiesel
Viscosity at 30 °C (c St)	D0445-04E02	3.06	69.6	5.72
Density (kg m^{-3})	D1298-99R05	860	911	885
Flash point (°C)	D0093-02A	76	230	170
Pour point (°C)	D0097-05A	−16	−3	−6
Cloud point (°C)	D2500-05	−10	0	−2
Carbon residue (%)	D0524-04	0.1	0.71	0.4
Ash content (%)	D0482-03	0.01	0.04	0.02
Sulfur content (%)	D129-00R05	0.05	–	0.02
Calorific value (kJ/kg)	–	42,490	38,416	37,425
Cetane number	D613-84	50	39	48

Nye and Southwel remaked that methanol/oil molar ratio of 6, in the presence of NaOH or KOH, yielded the satisfactory results [84]. Ahmad et al. optimized base catalyst for the transesterification of peanut oil. They concluded that 3.4% of NaOH was appropriate [26]. Meng et al. expressed that good yield of biodiesel from used cooking oil could be obtained by using methanol/oil molar of 6 and 1% NaOH with reaction time of 1 h [85].

Yuan Lin and Hsiu-Au prepared the biodiesel from soybean oil using methanol/oil molar ratio of 6 and 1% NaOH at 60 °C for 50 min. Then 1% hydrogen per oxide (H_2O_2) was added in the biodiesel and stirred in the reactor. The methyl ester was separated and washed with warm water to remove the un-reacted methanol and impurities. The methyl ester was tested in a four stroke, four cylinder engine and good results were found [86].

Zhang removed the moisture from the beef tallow before transesterification. They transesterified tallow by using methanol/oil molar ratio of 6 and 1% NaOH at 60 °C for 1 h. The methyl ester was re-transesterified using 20% methanol and 0.2% NaOH at 60 °C for 20 min. Methyl ester was washed and its properties were tested. They reported that conversion efficiency was 80% and the quality of biodiesel produced by two steps transesterification was better than that of biodiesel obtained by single step reaction [87].

Chitra et al., Kulkarni and Dalai, and Leung and Chen also transesterified different types of vegetable oils using sodium hydroxide and they obtained good results [88–90].

3.1.1.2. Sodium methoxide. Sodium methoxide ($NaOCH_3$) is more effective than sodium hydroxide as catalyst because it is disintegrated into CH_3O^- and Na^+ and does not form water in contrast to NaOH/KOH. Moreover its required amount is 50% as compared to sodium hydroxide [35]. But the catalyst is less common due to its higher cost.

Srivastava and Verma prepared sodium methoxide solution using 10 kg karanja oil, 28.5 g NaOH, and 2 kg methanol for transesterification. The reaction temperature was 70 °C and reaction time was about 1 h. After cooling, it was washed with 10% phosphoric acid solution. They obtained 84% conversion efficiency. They also tested the physical and chemical properties of biodiesel according to standards and compared them with those of diesel, as shown in Table 7.

Freedman et al. reported that 0.5% sodium methoxide and 1% sodium hydroxide exhibited similar results with methanol/oil molar ratios of 6 [92]. Dias et al. established the optimum amount of KOH, NaOH, and $NaOCH_3$ for soybean oil, sunflower oil, and used cooking oil. They concluded that 0.2–1% of any of these catalysts is needed for neat oil and 0.4–1.2% is needed for used cooking oil [53].

Li et al. transesterified glycerides using methanol/oil molar ratio of 5, in the presence of 0.6% sodium methoxide as catalyst. The reaction temperature was maintained at 55 °C and reaction time was half an hour. They obtained 97.25% conversion efficiency [93].

Rashid and Anwar transesterified safflower oil to convert it into biodiesel. They varied the methanol/oil molar ratio from 3 to 18,

reaction temperature from 30 °C to 60 °C and stirring speed from 180 to 600 rpm. They evaluated the performance of base catalysts (KOH, NaOH, $KOCH_3$, and $NaOCH_3$) and concluded that the best conversion efficiency could be obtained by using 1% of sodium methoxide (w/v) with methanol/oil molar ratio of 6 at reaction temperature of 60 °C, and stirring speed of 600 rpm. They did not report the optimum reaction time. The chemical and physical properties of biodiesel were also determined and found in accordance with (ASTM) D 6751 and EN 14214 specifications. Although they obtained 98% conversion efficiency, yet they did not carried out their experiments at temperatures higher than 60 °C. It was quite possible that the conversion efficiency might increase at higher temperatures [94].

Encinar et al. evaluated the performance of sodium hydroxide, potassium hydroxide, and sodium methoxide as catalysts using methanol. They varied the methanol ratio from 5 to 21% (by wt.) of cynara cardunculus oil, amount of catalyst 0.1–1% (by wt) and reaction temperature from 25 to 60 °C. They concluded that the biodiesel of best quality could be achieved by the use of 1% sodium methoxide and 15% methanol at 60 °C. They reported that the properties of the obtained biodiesel were very much similar to those of mineral diesel [95].

3.1.1.3. Potassium hydroxide (KOH). Potassium hydroxide is a base catalyst which is widely used in the transesterification process. Encinar et al. compared the performance of NaOH and KOH and reported that the performance of KOH was better than that of NaOH. They also reported that the separation of biodiesel and glycerol was easier when KOH was used as catalyst; hence it was preferred over NaOH [96]. Isigigur et al. transesterified safflower seed oil of Turkish origin using 1% KOH and obtained 97.7% methyl ester [97].

Tomasevic and Siler-Marinkovic converted sunflower oil and used cooking oil into biodiesel, using methanol in the presence of NaOH and KOH. They varied the methanol/oil molar ratio from 4.5 to 9 and KOH or NaOH from 0.5% to 1.5% of oil keeping reaction temperature at 25 °C for 30 min. They concluded that use of 1% of KOH and methanol/oil molar ratio of 6 at 25 °C returned the highest yield of best quality biodiesel in 30 min [98].

Refaat et al. optimized the parameters affecting the production of biodiesel. They used neat sunflower oil and waste vegetable oils as feedstock for biodiesel. They reported that more than 96% biodiesel could be obtained in 1 h by using 1% KOH and methanol/oil molar ratio 6 at 65 °C reaction temperature. They also reported that conversion efficiency was decreased by 1% when NaOH was used instead of KOH [55].

Rodjanakid and Charoenphonphanich transesterified palm oil stearin using 4 g of KOH and 200 ml of methanol per liter of oil at the temperature of 60 °C for 1 h. Magnetic stirrer was used to mix the materials homogenously. After the completion of reaction the methyl ester was separated from glycerol. The experiment was repeated by using 300 ml of ethanol and similar types of results were obtained. The methyl/ethyl ester was then washed, neutralized and tested in accordance with ASTM 6751 standards for physical and chemical properties. They reported that the results of methyl esters were better than those of ethyl ester [99].

Meher et al. performed a series of experiments to establish the adequate amount of KOH and methanol to convert the karanja oil into karanja methyl ester. They concluded that 1% KOH, methanol/oil molar ratio of 6, reaction temperature 65 °C, and reaction time of 2 h were the optimum values for transesterification reaction. They also reported that most of the reaction was completed within first 15 min; however 2 h were suitable to obtain maximum conversion efficiency (97–98%) [36].

Karmee determined the conversion rate of crude pongamia pinnata oil using methanol/oil molar ratio 10 in the presence of KOH as catalyst, at 60 °C and found 92% biodiesel. The conversion efficiency was increased to 95% when tetrahydrofuran (THF) was used as a co-solvent [100].

Tomasevic and Siler-Marinkovic performed a series of experiments and concluded that biodiesel of good quality could be obtained by using waste frying oil in the presence of 1% KOH and methanol/oil molar ratio of 6 at 25 °C for half an hour. They also reported that conversion efficiency could not be increased by increasing the amount of alcohol or catalyst [98]. Rao et al. and Mittelbach and Trathnigg also transesterified sunflower oil using KOH to produce sunflower oil methyl ester. They tested its physical and chemical properties and commented that the biodiesel could be used safely in compression ignition engines [101,102]. Higher conversion efficiency of biodiesel could be obtained with higher ratio of alcohol and KOH. Allawzi and Kandah displayed promising results using 300 ml ethanol and 1.2 g KOH for each liter of used soybean oil [103].

Dorado et al. converted Brassica carinata oil into methyl ester. They reported that methanol/oil molar ratio of 4.6 with 1.4% KOH at 20–45 °C, returned good results in 30 min. They also reported that the lower amount of KOH and extra amount of methanol were the causes of soap formation and reduced yield [104]. Antolín et al. converted sunflower oil using 0.28% KOH and two to three times excess amount of methanol than stoichiometric ratio at reaction temperature of 70 °C, and obtained more than 96% yield [105]. Hazelnut kernel oil was transesterified by Gumus, using methanol and KOH. He tested the hazelnut methyl ester in a diesel engine and encouraging results were reported [106].

3.1.1.4. Potassium methoxide. Potassium methoxide is a base catalysts which can also be used for transesterification reaction. Although it was tested by many researchers, yet very few recommended using it on regular basis. Casas et al. transesterified vegetable oil in the presence of KOH and CH_3OK, as catalyst. They compared the performance of these catalysts and reported that 99.2% yield was obtained in 1 h when 0.455% of CH_3OK was used with methanol to oil molar ratio of 8.5, and reaction time was 1 h. Whereas 98.1% yield was obtained in 3 h when 0.382% KOH was used with methanol to oil ratio of 11.3. No increase in conversion efficiency was observed in any case by increasing the amount of catalyst, methanol or time [63].

Encinar evaluated the performance of sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide as catalyst using ethanol. They varied ethanol/oil molar ratio from 6 to 12, amount of catalyst from 0.1 to 1.5% by wt., and temperature from 35 to 78 °C. They concluded that KOH was the most effective catalyst among the four catalysts; however the conversion efficiency using NaOH and CH_3OK was almost the same. The maximum conversion efficiency was about 75%, the reaction was completed at higher rate when CH_3OK was used instead of NaOH [107].

Vicente et al. compared the performance of sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide and concluded that the effects of all the four catalysts were similar in the transesterification reaction. All the experiments were conducted at temperature of 65 °C using methanol to sunflower oil molar ratio of 6 and amount of catalyst 1%. The results are shown in Table 8.

Rashid et al. converted cotton seed oil into biodiesel using sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide. It was resulted that 96% methyl ester was obtained with sodium methoxide, 89% with sodium hydroxide, 84% with potassium methoxide and 76% with potassium hydroxide in 2 h at 65 °C reaction temperature [108]. The yield of methyl ester, using these catalysts, for different reaction times is shown in Fig. 3.

Table 8
Effect of catalysts on the biodiesel purity and yield [43].

	Sodium hydroxide		Potassium hydroxide		Sodium methoxide		Potassium methoxide	
Biodiesel purity (wt.%)	99.70	99.7 ± 0.04	99.69	99.76 ± 0.05	99.70	99.72 ± 0.03	99.40	99.52 ± 0.10
	99.75		99.80		99.69		99.50	
	99.72		99.80		99.72		99.65	
	99.65		99.74		99.75		99.53	
Biodiesel yield (wt.%)	86.33	86.71 ± 0.28	91.67	91.67 ± 0.27	99.17	99.33 ± 0.36	98.33	98.46 ± 0.16
	86.67		91.67		99.33		98.50	
	87.00		91.33		99.83		98.33	
	86.71		92.00		99.00		98.67	

3.1.2. Heterogeneous base catalysts

Homogenous catalysts are very effective catalysts which are frequently used but the major problem associated with the use of these catalysts is their removal from methyl ester which needs excessive washing. A lot of energy, water, and time are consumed; moreover these catalysts cannot be reused. In contrast to that, the heterogeneous (solid) base catalysts being insoluble, are separated simply with filtration and can be reused many times. A lot of research has been done in this direction. Commonly used solid base catalysts are alkaline earth metal oxides, zeolite, KNO_3 loaded on Al_2O_3, KNO_3/Al_2O_3, BaO, SrO, CaO, MgO etc. [109,110]. Among the solid base catalysts BaO takes minimum time while MgO takes the maximum time to complete the reaction [111].

Ayhan reported that sunflower oil was converted into methyl ester at the temperature of 252 °C in about 30 min using 3% CaO and methanol to oil molar ratio of 41 [112]. Liu et al. used SrO as a solid base catalyst to convert soybean oil into biodiesel and achieved more than 95% conversion efficiency in just 30 min at a temperature of lower than 70 °C. They reported that the catalysts could be reused ten times effectively [113].

Liu et al. used calcium ethoxide as solid base catalyst which was prepared by reacting calcium and ethanol. They proposed the optimum condition as, methanol/oil molar ratio 12, calcium ethoxide 3%, and 65 °C reaction temperature. More than 95% soybean oil was converted into methyl ester within 90 min [114].

Kouzu et al. compared the performance of homogenous and heterogeneous base catalysts for the transesterification of soybean oil. The experiments were conducted using calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), and calcium carbonate ($CaCO_3$). The conversion efficiency was found to be 93% by using CaO, 12% by using $Ca(OH)_2$, and 0% by using $CaCO_3$ in 1 h. Since the use of CaO returned wonderful yield so further experiments were conducted using that catalyst by varying the reaction time, moisture contents, and feedstock of different characteristics. The results have been reproduced in Table 9.

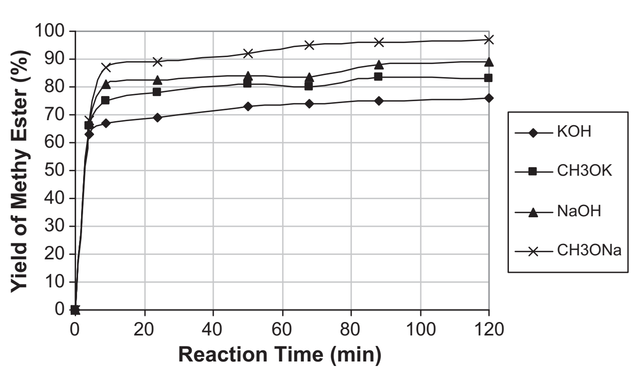


Fig. 3. Influence of catalyst type on the yield of cottonseed oil methyl esters (methanol/oil molar ratio of 6, temperature 65 °C, and rate of stirring 600 rpm).

3.2. Acid catalysts

Acid number is acidic functional group and measured in terms of quantity of potassium hydroxide required to neutralize the acidic characteristics of the sample [35].

Although the base catalysts are very efficient and popular for transesterification processes but these catalysts do not exhibit good results when the feedstock contains water contents and its acid value is high. Base catalysts are highly sensitive to water contents, which cause soap formation, and separation becomes difficult. The acid values of most of the non-edible oils are higher than the performance range of base catalysts. So, in such cases acid catalysts are used. But the problems associated with these catalysts are, requirement of higher amount of alcohol, higher reaction temperature and pressure, and slower reaction rate [9]. Reactor corrosion and environmental issues are also the hurdles in the use of acid catalysts [116].

Both homogenous and heterogonous acid catalysts can be used for transesterification. The acid catalysts which are more commonly used include, sulfuric acid, hydrochloric acid, phosphoric acid, and sulfonated organic acids.

The FFA of neat edible oils is normally low but these oils are costly and conversion of too much edible oil into biodiesel may cause food crises [117,118]. Hence the only choice is the use of waste oils or non-edible feedstock. The FFA of non-edible oils is generally high. FFA of edible oils is increased when these oils are used for frying purposes, due to hydrolysis of triglyceride. Acid catalysts are recommended to handle such feedstock. The acid value of some of the edible, non-edible, and used cooking oils is shown in Table 10.

Acid catalysts are generally used for two step transesterification. In the first step the oils are reacted with alcohol in the presence of acid catalysts. The acid value of the products is reduced and then the oil is re-reacted with methanol in the presence of base catalysts [102,124–127]. By this pretreatment the value of FFA decreases to alkaline transesterification range. Generally the value is reduced to

Table 9
Influences of free fatty acids, moisture, and polar fraction on transesterification of waste cooking oil (WCO) using calcium oxide [115].

	Composition (wt%)			Yield of FAME[a] (%)		
	FFA[b]	Moisture	Polars	0.5 (h)	1.0 (h)	2.0 (h)
SBO[c]	<0.1	<0.01	<0.1	62	93	>99
WCO[d]	2.6	0.05	18.7	0	66	>99
SBO-F[e]	2.5	<0.01	<0.1	0	76	>99
SBO-M[f]	<0.1	0.05	<0.1	49	95	>99
SBO-P[g]	<0.1	<0.01	15	54	97	>99

[a] By transesterifying at reflux of methanol.
[b] Free fatty acid.
[c] Edible soybean oil.
[d] Waste cooking oil with acid value of 5.1 mg-KOH/g.
[e] Edible soybean oil blended with free fatty acids extracted from WCO.
[f] Edible soybean oil with a dosage of distilled water.
[g] Edible soybean oil blended with polar fraction extracted from WCO.

Table 10
Acid value of edible and non-edible oils.

Edible oils	Acid value	Non-edible oils	Acid value
Rapeseed oil [39]	2.0	Rubber oil [119]	17.0
Coconut oil [80]	1.2	Karanja oil [35]	2.5
Soybean oil [119]	0.2	Tobacco oil [120]	35.0
Cotton seed oil [119]	0.1	Polanga oi [12]	22.0
Palm oil [80]	6.1	Jatropha oil [121]	14.9
Waste palm oil [39]	>20	Mahua oil [122]	19.0
Used frying oil [39]	5.6	Caster oil [123]	4.6

less than one. In the next step the oil is re-transesterified by using sodium or potassium hydroxide as catalyst [128]. The feedstock having higher value of FFA is recommended to be transesterified in two step fashion.

3.2.1. Homogenous acids

Dorado et al., Canakci and Gerpan, and Talens et al. converted the feedstock of higher acid value into biodiesel. They exercised a two step esterification. In the first step they used liquid acid and methanol for their esterification with which their acid value was reduced and then the oils were re-esterified using base catalyst [69,129,130].

Sahoo et al. transesterified the polanga oil in two steps. In the first step the oil was reacted with methanol in the presence of sulfuric acid and in the second step the fluid was transesterified by 1.5% KOH and methanol/oil molar ratio of 9, for 4 h. They optimized the amount of acid catalysts to reduce the acid value of polanga oil from 22% to 2%. They reported that 0.65% catalysts (98.4% anhydrous sulfuric acid) and methanol/oil molar ratio of 6 returned the best results in 4 h. It was then re-transesterified with methanol/oil molar ratio of 9 and 1.5% KOH for 4 h at 65 °C [12].

Wang et al. reported that the issue of high value of FFA could be tackled the by a two stage transesterification. In the first stage 2% w/w ferric sulfate and methanol/oil molar ratio of 10 was used for 4 h and the temperature was maintained at 95 °C. In the second stage NaOH of 0.5, 1, 1.5, 2, and 3 percent of oil was dissolved in methanol. It was then mixed with already esterified oil and stirred for 2 h at the temperature of 65 °C, and more than 97% methyl ester was achieved [65].

Puhan et al. converted linseed oil into biodiesel using 5% sulfuric acid and methanol/linseed oil molar ratio of 20 at 62–65 °C for 5 h. Then the biodiesel was washed with 5% salt water to reduce the PH value to neutral and product was dried in an oven, finally linseed oil methyl ester was found. They studied the chemical structure of linseed oil and compared its properties with linseed methyl ester. They tested this fuel in a single cylinder, four stroke, direct injection diesel engine, and found satisfactory results [131].

Ramadhas et al., Veljkovic et al. and Ghadge and Raheman reduced FFA of rubber oil (FFA 17), Tobacco oil (FFA 35) and Mahua oil (FFA 19) using acid catalyst. Their FFA was reduced to the range which was permissible for alkaline catalyst [119,120,122].

Although the acid catalysts are cheaper than base catalysts yet more amount of alcohol is needed when acid catalysts are used. Moreover, in the presence of acids in the reactants, the reactors of special material are required; hence the overall cost is increased [132]. Crabbe et al. transesterified crude palm oil using 5% sulfuric acid catalyst with methanol/oil molar ratio of 40. They conducted the experiments at the temperatures of 70 °C, 80 °C, and 95 °C and varied the reaction time. They concluded that reaction rate could be increased by increasing the reaction temperature. They reported that about 99.7% conversion efficiency was obtained in just 9 h at the reaction temperature of 95 °C and similar efficiency was obtained in 24 h at the temperature of 80 °C, using the similar amount and type of catalyst [67]. However, very low yield was returned at 70 °C even after 24 h. The results are shown in Fig. 4.

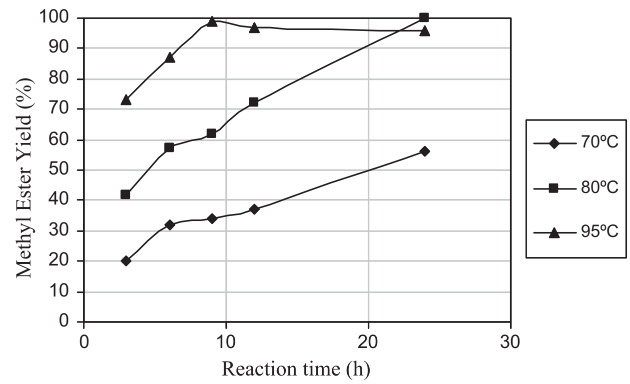


Fig. 4. Effect of reaction temperature and time on ester yield.

Miao et al. transesterified oil using trifluoroacetic acid as catalyst to covert vegetable oil into biodiesel directly by one step under mild pressure and temperature conditions. They reported that more than 98% yield could be obtained in about 5 h by employing 2.0 M catalysts concentration using methanol/oil molar ratio of 20 [133].

3.2.2. Heterogeneous acid catalysts

Heterogeneous acid catalysts are preferred over homogenous catalysts, because they do not dissolve in the alcohol and feedstock, hence they can be separated easily by filtration and can be reused. Such catalysts are effective for the esterification of FFA as well as of triglycerides, so their use is admired [134].

In 1996 Chavan et al. used super acid (SO_4^{2-}/SnO_2) as catalyst for esterification of ß Keto ester and obtained 97% conversion efficiency in 6 h [135]. In 2001 Chavan et al. used Amberlyst-15 and SO_4^{2-}/SnO_2 solid catalysts for esterification and they obtained the excellent results. They reported that Amberlyst-15 was cheaper and more effective for primary, secondary and allylic alcohols [136]. Matsuhashi et al. concluded that sulfated tin oxide ($SO4^{2-}/SnO$) have sufficient capabilities of esterification and strong acidity on the surface [137].

Zabeti et al. compared the performance of ZrO_2/SO_4^{2-} and ZrO_2/WO_3^{2-} and reported that conversion efficiency was 57% and 10% respectively [138]. Furuta et al. prepared solid super acid catalysts of tungstated zirconia–alumina (WZA), sulfated tin, zirconium oxides (SZA), and sulfated tin oxide (STO). They used them to transesterify the soybean oil with methanol at 200–300 °C. The catalysts showed high activities for the esterification and a very little amount of byproduct was found [139]. The results reported by them are reproduced in Fig. 5.

Some scientists developed sugar (sulfonated carbon) catalysts for the development of biodiesel and satisfactory results were

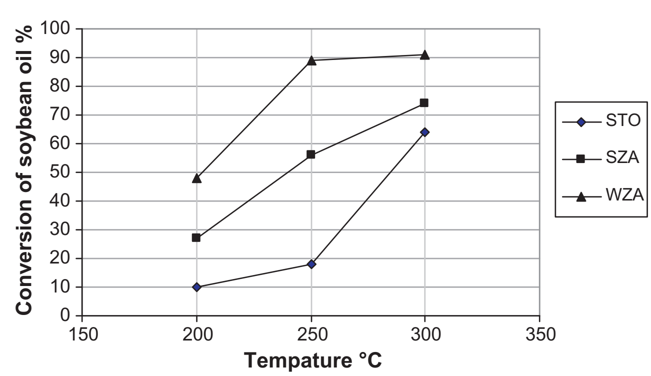


Fig. 5. Transesterification of soybean oil with methanol.

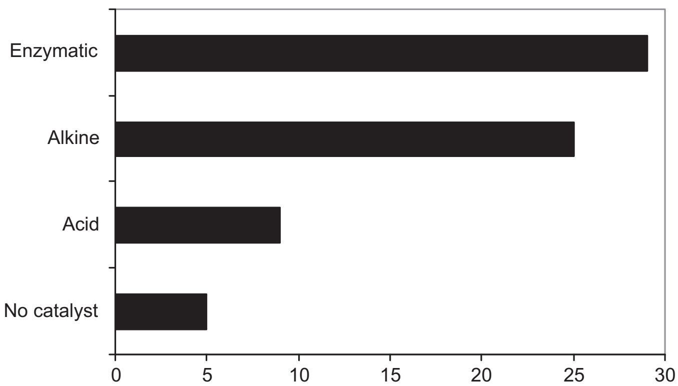


Fig. 6. Number of articles published in the year 2004 on transesterification using different catalysts.

reported. Such catalysts can be used to perform transesterification process at relatively lower temperatures [140–142]. Wang et al. compared the performance of sulfuric acid and ferric sulfate ($Fe_2(SO4)_3$) and reported that ferric sulfate exhibits better results as compared to sulfuric acid and it could be used in mild conditions [65].

3.3. Enzyme catalysts

The transesterification of vegetable oils or animal fats can also be carried out by using enzyme catalysts which are preferred because, by using them, soap is not formed; hence there is no problem of purification, washing, and neutralization. Another advantage of using enzymatic catalysts is that the reactions can be carried out at mild conditions. Enzymatic catalysts can also be applied on the feedstock of high FFA and converts more than 90% of oil into biodiesel. But the problems associated with enzyme catalysts are their higher cost and longer reaction time [143]. In spite of these problems interest is increasing in the use of enzymatic catalysts. For instance, in the year 2004, as shown in Fig. 6, twenty-nine researchers published their results who used enzymatic catalysts, whereas 25 used alkaline catalysts, and only 9 used acidic catalysts [144].

Athawale et al. transesterified soybean and linseed oil using lipases and concluded that the use of lipozyme as catalyst showed the excellent results for both the oils [145]. Jeong and Park converted rapeseed oil in 24 h using methanol/oil molar ratio of 3 at 40 °C temperature with 5% (w/w) Novozym 435 as catalyst. The conversion efficiency was more than 76%. Tert-butanol was added to restructure the effects of excess methanol [146]. Shah et al. performed transesterification of Jatropha oil using three different enzymes (i) Chromobacterium viscosum, (ii) Candida rugosa, and (iii) Porcine pancreas. They concluded that Chromobacterium viscosum was the best catalyst which returned 71% yield in 8 h. They also reported that yield could be increased to 92% using optimum conditions [147]. Liu et al. used Novozym 435, Lipozyme TLIM, and Lipozyme RMIM enzymes as catalysts to convert the stillingia oil into biodiesel in solvent-free and tert-butanol system [148]. Soumanou and Bornscheuer reported that lipase from Pseudomonas fluorescens with methanol/sunflower oil molar equivalent ratio of 4.5 could yield more than 90% biodiesel [149]. Nelson et al. reported that admirable results were found for transesterification of tallow using lipase from Mucor miehei with primary alcohols and Candida Antarctica with secondary alcohols. They also reported that similar type of results could be found for other feedstock of high FFA [150].

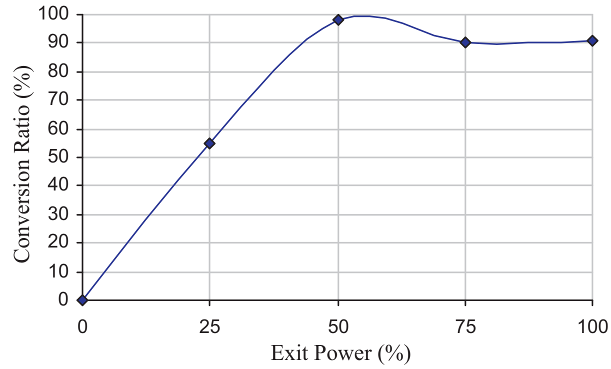


Fig. 7. Effect of microwave power level on transesterification of waste cooking oil.

4. Transesterification via radio frequency microwaves

Transesterification is also carried out using high frequency microwave irradiations. Microwave irradiations expedite the chemical reactions, reducing the time from hours to minutes and minutes to seconds. The microwave radiations mainly consist of infrared and radio waves. Generally the wavelength of microwaves lies between 1 mm and 1 m and frequency from 300 MHz to 300 GHz [151].

Refaat et al. transesterified used cooking oil using 20% methanol, 1% NaOH at 65 °C. The reaction was completed in 60 min and separation phase was completed in 8 h with conventional method. The process was repeated with same amounts of alcohol and catalyst using microwave irradiations. The reaction was completed within 2 min and separation phase was completed in 30 min. The conversion efficiency was 100%, as compared to 96% with that of conventional method [152]. Saifuddin and Chua produced ethyl ester using 0.5% NaOH, 100% excess anhydrous ethanol using microwave irradiation of 750 watts. They optimized the microwave exit power and reaction time. It was reported that the optimum reaction time was 4 min as compared to 75 min with usual transesterification method at 50% exit power of 750 W microwave [76]. The results are shown in Fig. 7.

Microwave assistated technique was used by Zhang et al. to convert yellow horn oil into methyl ester using heterogeneous catalyst. In this process 1% catalyst $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and methanol/oil molar ratio of 12 was used, and more than 96% oil was converted into biodiesel in 10 min. The catalyst is recyclable and can be used at least 9 times [153]. Microwave assisted transesterification process was also adopted by Yaakob et al. to convert the Jatropha oil and waste frying palm oil into their methyl esters. They optimized the parameters i.e., the amount of methanol and NaOH, and reaction temperature and time. They concluded that methanol/oil molar ratio 12, 1% NaOH, 65 °C reaction temperature, and 7 min reaction time is most appropriate. They obtained yields more than 88% in both cases [154]. Noureddini et al. and Krisnangkura and Simamaharnnop carried out the transesterification of various oils and reported that 1 min time is sufficient to complete the reaction for excellent conversion efficiency [155,156].

Lertsathapornsuk et al. used ethanol/waste frying palm oil ratio of 12 and 3.0% NaOH for half minute to convert the oil into 97% ethyl ester. Some modifications, as shown in Fig. 8, were made in the kitchen microwave oven of 800 watt, to use in this process. The properties of the ester were found exactly in accordance with the international standard AST 6751 [157].

Lertsathapornsuk et al. also performed intensive experiments assisted with microwave oven to optimize the amount of ethanol and reaction time using 1% NaOH. They concluded that yield of biodiesel was increased from 7.19% to 100% as the molar ratio of

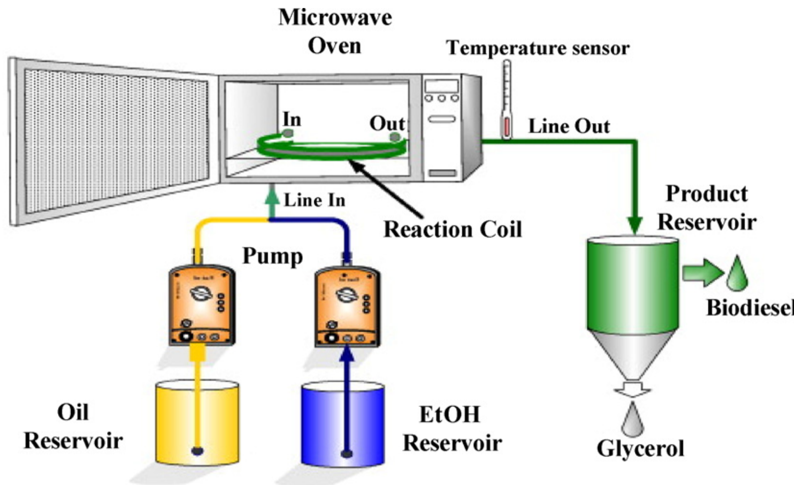


Fig. 8. Schematic diagram of continuous microwave reactor.

ethanol to the used cooking oil was increased from 3 to 9. The maximum yield (100%) was obtained in ten seconds when the alcohol to oil molar ratios were greater than 9. They also reported that chemical reaction did not depend on the reaction time but it depended on the oil/methanol molar ratio [158]. The results are shown in Table 11.

Stavarache et al. produced biodiesel using 28–40 kHz ultrasound. They reported that requirement of amount of catalyst is reduced from 50 to 66%, when ultrasound irradiations were used, while alcohol/oil molar ratio was the same as in the case of conventional method. The reaction time was decreased by increasing the frequency of ultrasound. However, the low frequency ultrasound returned better yield [159].

5. Transesterification using super critical methanol

Super critical methanol transesterification is a technique in which the feedstock is reacted with super critical methanol at extremely high pressure and temperature. With this technique the vegetable oils or animal fats can be converted into biodiesel with highly reduced time without the use of any type of catalyst. Due to the absence of catalyst, no washing and neutralization is required. Another merit of this process is that the water contents do not affect the reaction. However, the problem associated with this technique is the requirement of high pressure and temperature at which oil and supercritical methanol exist in the single phase.

Hawash et al. converted jatropha oil into methyl ester by conventional and super critical methanol methods. They reported that the reaction was completed in 4 min at 220 °C and 84 bars. The yield was 100% and the process was simple [160]. Kusdiana and Saka transesterified rapeseed oil using conventional and super critical methanol methods. They reported that maximum conversion efficiency could be obtained by applying methanol/oil molar ratio 42 via supercritical methanol treatment at the temperature of 350 °C and pressure of 300 bars for 6 min [161]. Demirba transesterified six different vegetable oils by conventional method and super critical methanol method. He reported that methanol/vegetable oil molar ratio 41 returned best yield (about 96%) at the temperature and pressure of 250 °C and 80 bars respectively. The reaction time was reduced from 2 h with conventional method to 220 s with super critical methanol method [33].

Yin et al. used co-solvent technique with super critical methanol at the temperature ranging from 260 °C to 350 °C, methanol/oil molar ratio was 42. They obtained more than 98% conversion of soybean oil. They also resulted that using 0.1% KOH in the reaction, temperature could be decreased to 160 °C [162]. Boocock et al. also used co-solvent technique using tetrahydrofuran and reaction was completed at moderate conditions and good yield was found [163].

Saka and Kusdiana prepared the methyl ester using rapeseed oil by super critical methanol (SC MeOH) method and compared it with conventional method [73]. The results are reproduced in Table 12.

Cao et al. transesterified soybean oil via supercritical methanol using methanol/oil molar ratio of 42, at temperatures of 350 °C and 400 °C and pressures of 450 and 650 bars. The good yield was obtained in 6 min. They also carried out the experiments using propane as co-solvent which caused to produce biodiesel at decreased temperature and pressure. The conversion efficiency was also improved [164].

Kusdiana and Saka compared the conversion efficiency of different oils using acid catalysts, base catalysts, and supercritical methanol [74]. The results are reproduced in Table 13.

Table 11
Conversion efficiency into fatty methyl ester by varying ratio of ethanol and reaction time.

Reaction time (s)	% Yield of fatty ethyl ester at different molar ratio					
	3:1	6:1	9:1	12:1	15:1	18:1
10	7.19	23.9	100	100	100	100
20	5.44	34.27	100	100	100	100
30	3.82	27.84	100	100	100	100
40	5.93	31.32	100	100	100	100
50	6.69	39.21	100	100	100	100
60	6.67	32.31	100	100	100	100
80	2.52	41.16	100	100	100	100
100	8.67	24.87	100	100	100	100

Table 12
Comparison between the conventional method and the supercritical methanol method for biodiesel production.

	Conventional method	SC MeOH method
Reaction time	1–8 h	120–240 s
Reaction conditions	1 bar, 30–65 °C	>80 bars and >239.4 °C
Catalyst	Acid or alkali	None
Free fatty acids	Saponified products	Methyl ester
Yield	Normal	Higher
Removal for purification	Methanol, catalyst and saponified products	Methanol
Process	Complicated	Simple

Table 13
Comparison of conversion efficiency of different feedstock with different methods.

Raw material	FFA content wt%	Water content wt%	Yields of methyl esters wt%		
			Alkaline catalyzed	Acid catalyzed	Supercritical methanol
Rapeseed oil	2.0	0.02	97	98.4	98.5
Palm oil	5.3	2.1	94.4	97.8	98.9
Used frying oil	5.6	0.2	94.1	97.8	96.9
Waste palm oil	>20.0	>61.0	No reaction	No reaction	95.8

6. Conclusions

- Vegetable oils and animal fats can be used to supplement mineral diesel oil. Fortunately no modifications in the engines are required to replace the diesel fuel with such fuels. These fuels are naturally grown and recyclable.
- Engines can be run on straight vegetable oil but for short terms only. To run it for longer time the properties of vegetable oils, or animal fats, and their chemical structure is required to be altered prior to use them in the compression ignition engines.
- Although, many means and ways are used to alter the chemical structure and the properties of vegetable oils, yet transesterification is more commonly used. It is an easy method and returns biodiesel of better quality.
- The conversion efficiency via transesterification depends upon many factors, e.g., type of feedstock, type and amount of alcohol and catalysts, reaction time, and reaction temperature.
- Mainly ethanol or methanol is used for tansesterification process. As methanol is cheaper, hence a vast majority of people use methanol. Moreover, the lesser quantity of methanol (66%) is used as compared to ethanol.
- The reaction temperature and reaction time depends upon type of catalyst, and type of processes. However, in general, reaction temperature is 55–70 °C and reaction time is 1–2 h for conventional catalysts and conventional processes.
- Catalysts play very important role in the development of biodiesel. Generally homogenous base catalysts are used. Most of the biodiesel producers use sodium hydroxide or potassium hydroxide. Although some researchers are of the view that sodium hydroxide is better than potassium hydroxide and some reported that potassium hydroxide is better than sodium hydroxide. But most of the authors are of the view that both sodium hydroxide and potassium hydroxide perform equally well.
- Sodium and potassium methoxides return better yield than all catalysts but they are costly, so they are not very frequently used. Heterogeneous or solid base catalysts are cheaper and more effective for the feedstock of higher value of FFA.
- Acid catalysts are preferred over base catalysts when feedstock contains moisture and having higher value of FFA. Both homogenous and heterogeneous acids are used for such oils. High reaction temperature and time is needed with the use of acid catalysts. Solid catalysts are insoluble in oil and alcohol, hence their separation is easy and they can be reused many times. However, the use of acid catalysts is environmental hazardous. In addition to that corrosion free reactor is needed when acid catalysts are used.
- Bio-catalysts (enzymes) are also used for transesterification but these are costly and they require longer reaction time. Hence these catalysts are not very frequently used.
- Transesterification can be highly expedited using radio frequency microwaves. Microwaves of 300 MHz to 300 GHz with wavelength of 1 mm to 1 m are generally used. This method is very fast and efficient. The conversion and settling time is magically decreased. The conversion time is reduced from 2 h to 4 min and settling time is reduced from 8 h to 30 min. No catalyst is required in this procedure and excellent quality of biodiesel is produced.
- Super critical methanol can also be used to expedite the transesterification. The conversion of vegetable oils into biodiesel is done in about 4 min but the extremely high pressure and temperature is required for this method. Therefore the reaction becomes highly sensitive and costly. A lot of energy is required to build such a high pressure and temperature. Use of co-solvent is also used to improve the conversion efficiency.

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